Canaigre Investigations

XI. Canaigre Root Tannin Makes Serviceable Leather*

By C. W. Beebe, W. S. Kip, W. F. Happich and J. S. Rogers

*Eastern Regional Research Laboratory***
Philadelphia 18, *Pennsylvania*

Previous papers on canaigre [1, 2, 3, 4, 5, 6, 7, 8, 9, 10] have reported various phases of the culture, analysis and extraction of the roots and on the production of canaigre-tanned leather by small scale tanning tests. The present paper deals with the production of enough canaigre-tanned leather for a practical wear test and the results obtained in that test.

There is a growing shortage of tanning materials in this country. The chestnut blight will eventually cause a shortage of the most important domestic tanning material. The development of canaigre as a tanning material is one of the attempts to remedy this situation. Canaigre has advantages over many other materials in that it contains a large amount of tannin, usually about 30 per cent (moisture-free basis), and that it may be grown as an annual or biennial crop instead of requiring many years of growth before utilization, as is the case with barks or woods. There are difficulties in the extraction of this material because of the presence of starch and some objections to its use in tanning because of the rather low purity of its tannin. Means for overcoming these difficulties have been described in previous papers.

The ultimate test of a tanning material must be a large scale test in a commercial tannery using standard methods. The large tonnage of canaigre extract necessary for such a test is not yet available; however, sufficient extract [7] was available to tan enough sole leather for a practical wear test by about 70 individuals. Mail carriers were selected as suitable "guinea pigs" for this test because they wear their shoes for long distances every day in all sorts of weather and because, by proper selection of the post offices, the shoes would be available for frequent inspections by laboratory personnel.

Tannage of Leather

The leathers used in this test were tanned from croupons or double bends. For comparison, a single bend from each croupon was tanned in a commercial tannery by its regular process, and the other single bend from the same croupon was tanned at the Eastern Regional Research Laboratory with a blend containing canaigre extract. The analysis of the extract is shown in Table I.

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**One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture.

TABLE I

Analysis of Canaigre Extract Used

	Per Cent
Total Solids	95.2
Soluble solids	92.1
Insolubles	3.1
Nontannin	31.7
Tannin	60.4
Purity tan sol. sol.	65.6
Total sugars	9.3
Reducing sugars	0.2

After the usual beamhouse treatment at the commercial tannery, 20 croupons were split along the backbone into single bends. Sixteen bends from the animal's right sides were tanned at the tannery by a commercial process using the usual commercial tanning blend. The remaining 24 bends were returned to the laboratory. These consisted of 16 left-side bends corresponding to the 16 right-side bends tanned at the tannery and 8 other bends, 4 left and 4 right. These 8 bends were used for a preliminary tannage, to partially mellow the liquors for the remaining bends.

The liquors used for the canaigre tannage at the laboratory were blends of 50 per cent canaigre, 25 per cent chestnut and 25 per cent sulfited quebracho liquors, calculated on a tannin basis. The vats held 3 single bends; the liquor to hide ratio was 8 to 1. A countercurrent press system of tannage was used, as similar as possible to that used in practice. The system was operated in such a manner that tail liquors contained 0.5 per cent tannin and the final head liquor 9 per cent. The tannage period was 6 weeks.

After the tannage at the laboratory, the leather was returned to the tannery, where all bends were finished simultaneously. All were then returned to the laboratory. Comparison of the canaigre and control leathers showed that the yield of the canaigre leather was slightly higher than that of the control leather, and the thickness somewhat greater. The yeields calculated from weight to finished weight were 70.7 per cent for the control bends and 73.3 per cent for the comparable canaigre bends. In comparing these with normal tannery yields, it should be kept in mind that these yields were obtained on the bend portions only. Thickness was measured at 20 selected points on each bend. The average thickness of the control bends was 8.5 irons; for the comparable canaigre bends it was 8.8 irons. Several practical tanners expressed the opinion that all leathers were entirely satisfactory in every respect.

Preparation of Test Shoes

The bends were matched into pairs; one that had been tanned at the tannery, the other from the same hide tanned at the laboratory with the canaigre

blend. Alternate right and left shoes were cut from each bend in such a way that a right sole was always matched with a left sole from a corresponding position on the bend from the opposite side of the animal. The thickness of each sole was measured. Each pair of soles was then numbered and stamped for permanent identification, and each pair was reserved for one pair of shoes. The soles, with the size specification for each pair, were then sent to a shoe factory, where low-cut, Garrison-type soes were made for the test. Included in this test were pairs of insoles for a test of alum retannage. A report on these insoles will be given later.

The Shoe Service Test

The shoes were distributed to the carriers in four post offices near the laboratory—the Chestnut Hill and Germantown Offices in Philadelphia and the Glenside and Hatboro Offices in nearby Montgomery County. Each carrier recorded the time of wear, miles traveled and other data as to comfort of shoes, etc. The shoes were inspected each week by laboratory personnel. When a hole appeared in either sole, the men ceased wearing the shoes, which were returned to the laboratory for resoling.

As some of the men left the mail service before the test was completed, only 65 pairs of shoes were returned for resoling and only 62 pairs were returned at the end of the test.

In resoling, the canaigre test sole was placed on the shoe opposite to that used for the first part of the test. This eliminated to a large degree the effect caused by greater wear on one shoe than the other. After a hole appeared in either of the second soles, the test for canaigre was considered complete, and all soles were removed for testing and analysis.

Evaluation of Results

The results were evaluated in two ways. The first consisted of a comparison of soles that failed first (Table II). To obtain a fair comparison of the canaigre and control soles, it was assumed that the soles showing equal wear should be divided equally between canaigre and control. This gave columns D and E. For the sum of the two tests, this showed 66 in favor of the canaigre and 61 in favor of the control, indicating a slight but possibly not significant superiority of the canaigre soles.

TABLE II

Relative Wear Based on Number of Soles Showing First Indication of Failure

	A Canaigre Superior	B Control Superior	C Equal Wear	D A+ ½ C	E B+ ½ C
First half of test	17	9	39	36½	28½
Second half of test	14	17	31	29½	32½
Total	31	26	70	66	61

This method does not take into account difference in wear between right and left feet in some individuals. To make allowance for this, all pairs of shoes were separated into the following seven categories. The wearing of the initial soles was taken as the first half of the test, and the wearing of the resoles as the second half.

1. In each half of the test, right and left shoes failed at the same time—13 pairs.
2. In each half, the right sole was better—12 pairs.
3. In each half, the left sole was better—8 pairs.
4. In each half, the canaigre sole was better—7 pairs.
5. In each half, the control sole was better—3 pairs.
6. In one half, the canaigre was better and in the other half both soles failed at the same time—8 pairs.
7. In one half the control was better and in the other half both soles failed at the same time—11 pairs.

Category 1 indicates equal wear of leathers; 4 and 6 indicate superiority of canaigre soles; 5 and 7 indicate superiority of control soles; in categories 2 and 3 any differences between the types of leather are obscured by the difference in wear between right and left feet. Table III shows the results. There are discrepancies between results in Table II and those in Table III because, for several reasons, some of the shoes worn in the first half of the test were not worn in the second half. Table III indicates a slight but hardly significant superiority of the canaigre over the control soles.

TABLE III

Relative Wear Based on Comparison of Failures in Each Half of Test

	Category	Number of Pairs
Equal wear of each type of leather in each half	1	13
Canaigre sole superior	4–6	15
Control sole superior	5–7	14
Indeterminate	2–3	20

In the second method of evaluation, the durability was measured by the loss in thickness during wear. The thickness of the worn sole was measured at the thinnest point. For soles not completely worn through, the thickness worn away was taken as the difference between the original thickness and the remaining thickness. For soles completely worn through, the remaining thickness was, of course, zero. The thickness worn away, however, cannot be taken as the original thickness. Confirming the work of Whitmore and Downing [11], [12], we have found that there is never complete abrasion throughout the entire

thickness. When a sole has worn down to a thickness of 0.05 to 0.10 cm., a hole will appear without further abrasion. Therefore, an arbitrary correction was made by subtracting 0.05 cm. from each measurement of soles completely worn through. The results (Tables IV, V and VI) show an average loss of thickness of 0.408 and 0.407 cm. for the first and second tests of canaigre soles, and 0.406 cm. for each test of the control soles. This difference is not considered significant. Although the correction for thickness of the soles completely worn through might be objected to as empirical, in this case it does not affect to any appreciable degree the comparison of the two types of leather.

TABLE IV

Wear of Soles

Loss in Thickness Measured in Thousandths of a Centimeter

Test I—Initial Soles

Shoe No.	Canaigre	Control	Shoe No.	Canaigre	Control	Shoe No.	Canaigre	Control
1	290	376	30	378	409	57	435	434
2	353	319	31	176	280	58	451	340
5	409	406	32	233	397	59	497	465
6	389	381	33	410	442	60	515	452
7	372	403	36	410	273	61	360	369
9	355	387	37	514	384	62	448	294
10	330	422	38	487	497	63	436	398
11	394	380	39	436	512	64	443	440
12	354	361	40	513	363	65	324	423
13	432	367	41	472	361	66	413	393
15	421	267	42	444	410	67	453	309
16	439	407	43	394	384	68	416	455
17	426	419	44	464	468	69	401	411
18	528	431	46	509	538	70	367	503
19	454	412	48	491	476	73	463	409
21	507	460	50	325	330	74	265	465
23	441	408	51	487	396	75	480	471
24	436	441	52	318	391	77	398	452
26	430	406	53	502	500	78	359	356
27	450	274	54	413	381	79	465	455
28	234	400	55	401	408	80	367	508
29	250	451	56	377	408			
					Total		26544	26388
					Average		408	406

A record of the number of hours the shoes were worn and the mileage covered was obtained. There was little correlation between these. The mileage was the distance covered on deliveries, whereas the hours covered the total time worn, including time for sorting. It would be difficult to estimate the

TABLE V

Wear of Soles
Loss in Thickness in Thousandths of a Centimeter
Test II—Resoles

Shoe No.	Canaigre	Control	Shoe No.	Canaigre	Control	Shoe No.	Canaigre	Control
1	184	429	30	403	512	56	439	306
2	396	300	31	448	457	57	409	428
6	462	471	32	445	325	58	291	503
7	450	434	33	531	427	59	237	448
9	424	329	36	297	451	60	398	426
10	484	344	37	494	431	61	235	448
11	438	402	38	443	447	62	443	494
12	415	392	39	412	331	63	385	385
13	359	376	40	420	355	64	414	452
15	407	419	41	431	445	65	401	325
16	395	410	42	372	346	68	425	405
17	373	435	43	428	354	69	308	393
18	456	400	44	477	525	70	420	337
19	506	479	46	460	353	73	409	434
21	362	396	48	444	293	74	433	371
23	429	455	50	438	398	75	459	373
24	483	475	51	314	388	77	448	422
26	402	442	52	453	371	78	395	320
27	243	439	53	476	494	79	412	406
28	465	433	54	314	366	80	453	301
29	354	407	55	428	438			
					Total		25,229	25,151
					Average		407	406

TABLE VI

Summary of Tables IV and V
Average Thickness of Leather Worn Away

	Canaigre cm.	Control cm.
Initial soles	0.408	0.406
Resoles	0.407	0.406
Total	0.408	0.406

amount of wear on the shoes during the periods when no deliveries were being made.

There were large differences between individuals in the time required to wear out the soles and the mileage covered. The time of wearing ranged from 74 to 2130 hours, and the mileage from 100 to 1850 miles. The average time required was 320 hours, and the average mileage as reported was 290 miles.

For the reasons already given, it is believed that these figures are highly inaccurate and of little significance.

Although accurate records of hours worn and mileage covered would have been interesting, lack of these figures does not vitiate the results in any way, because the test was intended primarily to give a direct comparison of two types of leather used under the same conditions.

A record was made of the weight of the men in an attempt to correlate this with wear of the shoes. As expected, there was little correlation. Although the weight of the man may be one of the factors influencing wear, other factors are more important. For example, a man weighing 190 pounds wore his shoes without failure for 1196 hours, whereas a man weighing 135 pounds wore his shoes for only 206 hours without failure.

The figures obtained by the analysis of the original and worn leathers (Table VII) indicate that there is no significant difference between the analyses of the two original leathers. In comparing the analyses of the original and worn leathers, it must be kept in mind that the analysis of the worn leather is not that of the whole leather but only of that remaining after a large part of the thickness of the leather has been worn away from the grain side. This should have a tendency to increase the amount of hide substance and decrease the amount of combined tannin. As there is actually an increase in the amount of combined tannin, there is some indication that there has been a change resulting in a firmer combination of tannin and hide substance. The increase in insoluble ash and oil during wear is due to sand and tar picked up from driveways. There is a aloss of soluble solids during wear.

TABLE VII

Analyses of Leather

	Canaigre		Control	
	Before Wear	After Wear	Before Wear	After Wear
Oil, %	6.6	9.5	6.6	11.5
Insoluble ash, %	0.7	1.6	0.7	1.6
Hide substance, %	37.9	43.0	37.4	43.0
Soluble matter, %	30.4	18.5	30.7	17.5
Combined tannin, %	24.4	27.4	24.6	26.4
Total	100.0	100.0	100.0	100.0
Degree of tannage	64.4	64.0	65.6	61.7
Uncombined nontannin	19.9	8.8	19.2	8.5
Uncombined tannin	10.5	9.6	11.5	9.1
Glucose	5.8	2.3	5.2	2.2
Total ash	7.1	4.0	7.4	3.8
Epsom salts	7.8	2.9	8.9	2.3
pH	3.4	3.9	3.4	3.9

Almot all the men reported that the shoes were comfortable. A few complaints had no correlation with the type of leather used.

Conclusions

Within the limits of experimental error, the wear of leather tanned with a canaigre blend is equal to that of normally tanned leather.

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References

1. Canaigre Investigations IX. Laboratory Tannage of Heavy Leather. C. W. Beebe, W. S. Kip, II, and J. S. Rogers. *J. Amer. Leather Chemists Assoc.*, **46,** 197 (1951).
2. Canaigre Investigations III. An Improved Method of Extraction. T. C. Cordon, C. W. Beebe, and J. S. Rogers, *ibid*, **42,** 118 (1947).
3. Canaigre Investigations IV. Fermentation of Liquors for Production of High Purity Extracts. T. C. Cordon, C. W. Beebe, and J. S. Rogers. *ibid*, **42,** 128 (1947).
4. Canaigre Investigations VII. Fermentation of Extract Liquors and Identity of the Bacteria and Products of Their Growth. T. C. Cordon. *ibid*, **45,** 485 (1950).
5. Canaigre Investigations V. Analytical Studies on the Extraction of Canaigre Roots with Water and with Acetone–Water Mixtures. F. P. Luvisi and J. S. Rogers, *ibid*, **43,** 166, (1948).
6. Canaigre Investigations VI. Extraction with Organic Solvent-Water Solutions. F. P. Luvisi, T. C. Cordon, C. W. Beebe, and J. S. Rogers. *ibid*, **44,** 707 (1949).
7. Canaigre Investigations VIII. Preparation of Tanning Extracts by Continuous Countercurrent Extraction. R. M. Rieder, N. F. Roger, G. W. M. Phillips and R. K. Eskew. *ibid*, **46,** 188 (1951).
8. Countercurrent Stationery Vat Leaching of Shredded Canaigre Roots, R. M. Rieder, V. A. Turkot, R. K. Eskew, and G. W. M. Phillips, *ibid*, **46,** 264, (1951).
9. Canaigre Investigations I. A Review and Preliminary Report. J. S. Rogers and G. A. Russell, *ibid*, **39,** 467 (1944).

10. Canaigre Investigations II. Dehydration of Bulk Lots of Canaigre Roots in the Locality Where Harvested. G. A. Russell, J. S. Rogers, and E. C. Stevenson. *ibid*, **39**, 479 (1944).
11. Practical Wearing Tests in Sole Leather. L. M. Whitmore and G. V. Downing. *ibid*, **37**, 150 (1942).
12. Note—Practical Wearing Tests in Sole Leather. L. M. Whitmore and G. V. Downing, *ibid*, **39**, 72 (1944).